

with each other, and also boron oxide 4 and raw material 2 were brought into contact with each other when the raw material was melted.

This crucible 1 was inserted in a quartz ampoule 5 together with solid arsenic. Quartz ampoule 5 was sealed under reduced pressure using quartz cap 6.

Respective conditions of example 4 are indicated in the following Table 7.

TABLE 7

GaAs polycrystalline raw material	3 kg used
Carbon disk	Diameter 30 mm, thickness 10 mm used Heat treatment at 1500° C. for 12 hours at the pressure of 1 Torr
B <sub>2</sub> O <sub>3</sub>	Water concentration 300 wt ppm, 50 g used
pBN crucible	Inner diameter 80 mm, entire length 250 mm
Solid arsenic	1 g used

The above-described quartz ampoule 5 was heated at the rate of approximately 200° C./hour by heater 8 using vertical furnace 50.

During the process of heating, boron oxide 4 was softened and melted. Also, GaAs polycrystalline raw material 2 was melted.

At this time point, boron oxide 4 was present as a film 4a having a thickness of less than 1 mm between pBN crucible 1 and GaAs melt 2. The remainder of boron oxide 4 covered the upper surface of GaAs melt 2. The thickness of the boron oxide layer 4b covering the upper surface of GaAs melt 2 was approximately 6 mm. Carbon disk 43 had its bottom surface in contact with raw material melt 2, and its top surface exposed to the ambient. The side surface thereof was surrounded by boron oxide layer 4b.

The condition mentioned above was kept for approximately 6 hours.

Then, heater 8 was moved upwards at the rate of 4 mm/hour, whereby solidification started from the portion of seed crystal 7. Thus, a single crystal was grown. The characteristics of the obtained single crystal are shown in the following Table 8.

TABLE 8

Crystal diameter	80 mm	
Length of Ø80 mm portion	100 mm	
Carbon concentration	Shoulder	$6.8 \times 10^{15} \text{ cm}^{-3}$
	Tail	$7.1 \times 10^{15} \text{ cm}^{-3}$
Resistivity	Shoulder	$4.5 \times 10^6 \Omega\text{cm}$
	Tail	$5.2 \times 10^6 \Omega\text{cm}$
Dislocation density	Shoulder	$1200 \text{ cm}^{-2}$
	Tail	$1500 \text{ cm}^{-2}$

In a semi-insulating GaAs crystal, the resistivity is one of the most important characteristics. It is preferable that variation in resistivity is smaller. Furthermore, since this resistivity value depends on the carbon concentration in the GaAs crystal, variation in the carbon concentration in the crystal should be as small as possible.

In the above-described examples where carbon fiber or bulk carbon was used as the solid carbon, the carbon was doped substantially uniformly from the shoulder to the tail of the crystal. It is appreciated that carbon fiber and bulk carbon are preferable as solid carbon sources. The shape of bulk carbon is not limited to the disk shape shown in Example 5, and any shape can be used. Also, bulk carbon is preferably a sintered compact of carbon powder.

Comparison of the effect of the present invention depending upon difference in the type of solid carbon is shown in the following Table 9.

TABLE 9

Difference in effect among powder, fiber, and bulk carbon	
Type of solid carbon	Carbon distribution in a crystal from shoulder to tail
Carbon powder	Gradual decrease of carbon from shoulder to tail
Carbon fiber	Uniform distribution of carbon from shoulder to tail
Bulk carbon	Uniform distribution of carbon from shoulder to tail

Comparison of the carbon concentration in a GaAs crystal between the present invention and the prior art is shown in the following Table 10.

TABLE 10

Comparison of carbon concentration in GaAs crystal			Carbon concentration ( $\text{cm}^{-3}$ )	
			Shoulder	Tail
Present invention	Carbon powder	Example 2	$1.4 \times 10^{15}$	$0.8 \times 10^{15}$
		Example 3	$9.5 \times 10^{15}$	$7.0 \times 10^{15}$
		Example 4	$2.3 \times 10^{15}$	$2.2 \times 10^{15}$
		Example 4	$1.3 \times 10^{15}$	$1.2 \times 10^{15}$
Prior art	Carbon disk	Prior art 2	$6.8 \times 10^{15}$	$7.1 \times 10^{15}$
		Prior art 3	$0.5 \times 10^{15}$	$0.4 \times 10^{15}$
		Prior art 3	$2.2 \times 10^{15}$	$1.4 \times 10^{15}$

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

What is claimed is:

1. A method of preparing a carbon-doped group III-V compound semiconductor crystal, comprising the steps of: placing a compound raw material, solid carbon, and a boron oxide substance into a crucible or a boat, sealing said crucible or boat containing said compound raw material, said solid carbon, and said boron oxide substance within an airtight vessel formed of a gas impermeable material, heating and melting said compound raw material in said crucible or said boat sealed within said airtight vessel, and solidifying said melted compound raw material to grow a carbon-doped compound semiconductor crystal, wherein an amount of said solid carbon placed into said crucible or said boat is larger than an amount of carbon doped into said compound semiconductor crystal.
2. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1, further comprising a step of heating and melting said boron oxide substance and having said melted boron oxide substance in contact with at least a portion of said solid carbon, during said step of heating and melting said compound raw material.
3. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1,

wherein said gas impermeable material comprises a material selected from the group consisting of quartz and pBN.

4. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1, wherein said boron oxide substance comprises boron oxide and water.

5. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 4, wherein said boron oxide substance contains 10-500 wt ppm of said water.

6. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1, wherein said amount of said solid carbon placed into said crucible or said boat is at least 10 times larger than said amount of carbon doped into said compound semiconductor crystal.

7. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1, further comprising a step of subjecting said solid carbon to a heat treatment under reduced pressure before placing said solid carbon into said crucible or said boat.

8. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 7, comprising carrying out said heat treatment for 1 hour to 12 hours at a temperature of 500° C.-2000° C. under a pressure of 1 Torr - $1 \times 10^{-8}$  Torr.

9. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1, further comprising a step of maintaining said melted compound raw material in a melted state for a certain time period before said step of solidifying said melted raw material to grow said crystal.

10. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 9, wherein said step of maintaining said melted compound raw material in a melted state is carried out for 3-72 hours.

11. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1, wherein said solid carbon comprises powder carbon.

12. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 11, wherein said powder solid carbon has a grain size of not more than 100  $\mu$ m.

13. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1, wherein said solid carbon comprises fiber carbon.

14. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 13, wherein said fiber solid carbon has an average diameter of not more than 50  $\mu$ m.

15. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1, wherein said solid carbon comprises bulk carbon.

16. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 15, wherein said bulk carbon has a disk shape with a disk diameter smaller than an inner diameter of said crucible.

17. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 15, wherein said bulk carbon comprises a sintered compact of carbon powder.

18. A method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1, wherein said crucible or said boat comprises pBN.

19. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1, wherein said compound raw material comprises GaAs, and wherein said compound semiconductor crystal comprises a GaAs crystal.

20. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 2, further comprising having said melted boron oxide substance in contact with at least a portion of said melted compound raw material, during said step of heating and melting said compound raw material.

21. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1, further comprising selecting a target amount of said carbon to be doped into said compound semiconductor crystal, and adjusting said amount of said solid carbon placed into said crucible or said boat so as to responsively achieve said target amount of said carbon to be doped into said semiconductor crystal.

22. The method of preparing a carbon-doped group III-V compound semiconductor crystal according to claim 1, carried out such that said carbon-doped compound semiconductor crystal has a variation of carbon concentration of not more than 8 1/2% between a lowest carbon concentration and a highest carbon concentration, relative to said lowest carbon concentration.

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23. A charge for use in vertical boat growth of GaAs single crystal ingots comprising: poly-crystal GaAs material; a source of carbon; and Boron Oxide wherein said source of carbon comprises carbon powder; the nominal doping potential of said carbon powder included in the charge is large compared to the planned target level of carbon dopant in an as grown ingot, and said Boron Oxide is provided in an amount for providing spacer material between an as grown ingot and a crucible wall, and between a seed crystal and the bottom of said crucible.

24. A charge in accordance with claim 23 wherein the nominal doping potential of said carbon powder included in the charge is the order of 100 times the planned target level of carbon dopant in an as grown ingot.

25. A charge in accordance with claim 23 wherein the nominal doping potential of said carbon powder included in the charge is at least several times the planned target level of carbon dopant in an as grown ingot.

26. Vertical boat growth of single crystal, semi-insulating GaAs ingots having controlled planned target levels of Carbon therein comprising: (a) loading a crucible with a charge of poly-crystal GaAs material; a source of carbon; and Boron Oxide over a selectively oriented seed crystal; (b) placing said crucible in a closed quartz tube; (c) applying a controlled pattern of heating to melt the charge and a portion of the seed crystal to sequentially freeze the melt starting at the interface with the seed crystal to form a single crystal; wherein said source of carbon is carbon powder in a selected

quantity having a defined large nominal doping potential compared to the planned target level of Carbon in an as grown ingot; and said Boron Oxide is provided in an amount for providing spacer material between an as grown ingot and a crucible wall, and between a seed crystal and the bottom of said crucible.

27. Vertical boat growth of single crystal, semi-insulating GaAs ingots in accordance with claim 26 wherein said pattern of heating comprises: heating said charge to the melting point temperature of GaAs; holding that temperature for a period of time.

28. Vertical boat growth of single crystal, semi-insulating GaAs ingots in accordance with claim 26 wherein the nominal doping potential of said carbon powder included in the charge is the order of 100 times the planned target level of carbon dopant in an as grown ingot.

29. Vertical boat growth of single crystal, semi-insulating GaAs ingots in accordance with claim 26 wherein the nominal doping potential of said carbon powder included in the charge is at least several times the planned target level of carbon dopant in an as grown ingot.

30. Semi-insulating mono crystalline GaAs material produced in accordance with any of claims 26, 27, 28 or 29.

31. The method of any of claims 1 - 22 wherein sufficient boron oxide substance is placed in said crucible or boat so that the boron oxide substance surrounds the melted semiconductor compound.

32. The method of claim 31 wherein said melting and solidifying is conducted in a vertical furnace.

33. The method of any of claims 1 - 22 wherein said melting and solidifying is conducted in a vertical furnace.

34. The method of any of claims 2 - 10 or 18 - 22 wherein said solid carbon is powdered carbon.

35. The method of claim 34 wherein sufficient boron oxide substance is placed in said crucible or boat so that the boron oxide substance surrounds the melted semiconductor compound.

36. The method of claim 34 wherein said melting and solidifying is conducted in a vertical furnace.

37. The method of any of claims 2 - 10 or 18 - 22 wherein said solid carbon is carbon fibers.

38. The method of claim 37 wherein sufficient boron oxide substance is placed in said crucible or boat so that the boron oxide substance surrounds the melted semiconductor compound.

39. The method of claim 37 wherein said melting and solidifying is conducted in a vertical furnace.